



## Dynamic conductivity measurements in humic and fulvic acid solutions

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### Abstract

Conductivity changes of dilute aqueous humic and fulvic acids solutions were monitored after the addition of small quantities of Cu, Cd, Pb, and Zn. The solutions were stirred at a constant and reproducible rate, and measurements proceeded until stable conductivities were attained. The values were compared to KCl reference solutions treated in an identical manner, and the results showed that the humic materials significantly reduced metal ion mobilities. Pb and Cu were affected more than Cd and Zn, and especially Zn regained a significant portion of its mobility upon dispersal. Cu, in contrast, was strongly and irreversibly retarded in all cases. It was inferred that Zn underwent transient electrostatic interactions with humics at high local concentration, while associations between Cu and humics were rapid and permanent. Different humic materials showed these effects to different extents. Raising the temperature from 20 to 60 °C did not, as expected, lead to higher relative conductivities in metal–humate solutions, but showed enhanced retardation of the cations. It was noted that temperature induced aggregation (clouding) of humic solutions increased the effective sizes of the metal–humate complexes, reducing their mobilities in aqueous solution. © 2003 Elsevier B.V. All rights reserved.

**Keywords:** Humic and fulvic acids; Dynamic conductivity; Ionic mobility; Aggregation; Polyanion size; Dispersal

### 1. Introduction

Conductivity measurements have been used only infrequently in the study of aqueous humic materials. The studies that employed conductometric techniques have focused almost entirely on titrations aimed at determining the acidities of dissolved humic and fulvic acids. Early work in this field has been discussed by Flaig et al. [1], who noted that the titration curves often had several breaks, whose number and position depended on the titrant used. They also touched on the influence of metal–humate complexation on electrophoretic properties of humic acid (HA) solutions and concluded that the complexes formed were generally negatively charged and moved toward the anode. Gamble [2] used conductometric titration data as supporting evidence in the calculation of dissociation constants of fulvic acid (FA). He found that the conductivity measurements, taken in FA solutions without a background electrolyte, gave results in

remarkable agreement with those obtained by potentiometric titrations in FA solutions containing 0.1 M KCl.

Arai and Kumada [3,4] carried out a series of conductometric replacement titrations, in which the HA solutions were titrated with standard acid after addition of an excess of base. This allowed them to determine the total acidities of the humates, and also to quantify three clusters with different dissociation constants among the acid functionalities. Riggle and von Wandruszka recently reported that the slopes of replacement titration curves could be related to the sizes of humic aggregates in solution [5].

The study of humic solutions by conductometric means is possible because the dissolved humates carry a negative charge, mostly due to dissociated carboxyl moieties, and therefore move in an external electric field. The motion of a singly charged ion is determined by a simple force balance involving the electric field and the viscous resistance of the solution.

$$eE = 6\pi\eta rv \quad (1)$$

Here  $E$  designates the electric field,  $e$  is the electronic charge,  $\eta$  is the solution viscosity,  $r$  is the ionic radius, and  $v$  is the

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velocity of the ion. Based on this Stokes law expression, the ionic mobility,  $u$ , is defined as

$$u \equiv \frac{v}{E} = \frac{e}{6\pi\eta r} \quad (2)$$

The primary measured parameter in a conductometric experiment is the conductance,  $L$ , which is the reciprocal of the solution resistance and has the units of Siemens (S, i.e.  $\Omega^{-1}$ ). The intrinsic solution property is the conductivity,  $\kappa$ , with units of  $S\text{ cm}^{-1}$  such that

$$\kappa = L \frac{l}{A} \quad (3)$$

where  $A$  is the cross-sectional area of the electric field,  $l$  is its length, and the quantity  $l/A$  is the cell constant. The ionic conductivity,  $\lambda$ , which is related to the ionic mobility through Faraday's constant ( $\lambda = Fu$ ), is therefore inversely related to the size of the aqueous ion. This has immediate bearing on the shape and configuration of humic and fulvic polyanions in solution. The representation of aqueous humic materials as long, charged polymer chains has served well in the past to explain their behavior in solution [6]. Dilute salt-free solutions of such polyelectrolytes are generally modeled as rod-like chains of quasi-spherical electrostatically-bound assemblies, referred to as *blobs* [7]. At higher polyanion concentrations (semidilute solutions), a correlation length,  $\xi$ , is defined, beyond which the chain assumes a random walk configuration. This results in a randomly folded arrangement of the corresponding segments, each of which contains several electrostatic blobs in a rigid disposition. The presence of salt in such a solution leads to enhanced electrostatic screening of the polymer charges by the salt ions, effectively reducing the Debye electrostatic screening length,  $r_D$ , of the system. The scaling theory of such polyelectrolyte solutions is well developed [8], and their conductivity behavior is reasonably well understood [9]. As regards the application of this model to dissolved humates, however, recent findings have cast doubt on the representation of these entities as long polymer chains [10–12]. The view has emerged that the aqueous species consist of aggregates of smaller units held together by a variety of bonding interactions, including metal bridging. The chief difference between this concept and the older model lies in the compositional detail (especially “monomer” size) of the overall structure. This structure may still be looked upon as a roughly spherical aggregate of polyanionic species, which becomes self-averaging at this scale.

The molar conductivity of a dilute humic solution containing no added salt can be approximated by the simple expression

$$\Lambda = f(\lambda_h + \lambda_c) \quad (4)$$

where  $\lambda_h$  is the ionic conductivity of the humic polyanion, and  $\lambda_c$  is the ionic conductivity of the counterion. The factor  $f$  is a fractional parameter that accounts for the partial association between humate and counterion. The polyanion

conductivity  $\lambda_h$  is fundamentally a composite quantity because of the intrinsic polydispersity of humate, while  $\lambda_c$  also contains contributions from various cations that may be associated with the humic material. The chief anionic group on HA is the carboxyl group, which, after the customary isolation and purification procedures, will yield mostly  $H^+$  as the counterion. Alkaline earth and alkali metals (especially if a hydroxide like NaOH was used to solubilize the HA) will also be present.

Addition of salt to dilute aqueous HA contributes further counter- and co-ions to the solution and affects the configuration of the humic polyanion. In solutions of low ionic strength, the humate is best represented as a porous sphere made up of various associated units [5]. This corresponds to the expanded form of the aqueous polyion described by the IUPAC Commission on Electroanalytical Chemistry [13]. All counter-cations in such a system interact with the polyanion: some are electrostatically trapped (condensed) within the porous sphere, while others form a diffuse cloud around it. It has been suggested by Overbeek [14] that co-ions may be considered to behave independently from the polyions.

The conductivity,  $\kappa$  of a dilute HA solution at low ionic strength may be generalized in the form

$$\kappa = \sum_h z_h f_h \lambda_h c_h + \sum_i z_i f_i \lambda_i c_i + \sum_j z_j \lambda_j c_j \quad (5)$$

where  $h$  refers to humate,  $i$  to counterion, and  $j$  to co-ion;  $f_h$  and  $f_i$  are the charge fractions of humate and counterion available to conduct current,  $c$  denotes the analytical concentration, and  $z$  is the ionic charge.

The contribution of the humic polyanion to  $\kappa$  is best approached through the ionic mobility,  $u_h$ , of the species. For the case of a multi-charged humic aggregate in the form of a porous sphere with negligible drainage, Eq. (2) becomes

$$u_h = \frac{|z_h|e}{6\pi\eta r_h} \quad (6)$$

where  $r_h$  is the radius of the polyanionic assembly and  $z_h$  is its charge.

The prime goal of the work described below was not the determination of the conductivity of humic solutions per se, but rather the influence of the polyanions on the solution conductivity contributed by added cations. It was the aim of the investigation to relate measured conductivity changes to progressive metal–humate associations. To this end, small aliquots of a salt solution were added to dilute aqueous humates and fulvates under constant stirring. The development of the solution conductivity was monitored and related to the status of the ionic species present. To account for the various influences, it is instructive to conduct a thought experiment involving two different HA solutions, prepared in the same manner. To each of these solutions identical small aliquots of, for instance, a  $CuCl_2$  solution is added under the same stirring regimen. If the mixing process following the addition is sufficiently reproducible to eliminate it as a source of difference in conductivity development in the two

solutions, then the interactions between  $\text{Cu}^{2+}$  and the humic polyanions are the principal cause of possible variations in solution conductivity. Eq. (6) shows that the size of the humic anion, through radius  $r_h$ , influences its mobility in aqueous solution and hence its contribution to the overall conductivity. Since the co-ion conductivity will be similar in the two solutions, the other important factor is  $f$  (both as  $f_h$  and  $f_i$ ). This is related to the association between polyanion and added counterion ( $\text{Cu}^{2+}$ ), and may be looked upon as a relaxation effect connected to the retardation caused by an asymmetry of charge distribution around the polyanion in an electric field [12]. The amount of cation added is the same in both humic solutions, so any difference in conductivity response must be primarily determined by the available association sites (mostly carboxylate) of the humate and their accessibility to the counterion.

The addition of  $\text{CuCl}_2$  will necessarily lead to an increase in conductivity of both HA solutions under consideration. Possible differences between the solutions could arise from two effects: (i)  $\text{Cu}^{2+}$  association with humate that is greater in one solution than in the other, and effectively makes  $f_h$  and  $f_i$  smaller in the less conducting solution; (ii) the formation of Cu–humate complexes that makes the polyanionic assemblies shrink/expand to different extents in the two solutions, affecting their mobilities.

## 2. Experimental

### 2.1. Humic materials and reagents

Minnesota peat fulvic acid (MNPFA), soil humic acid (SHA), and nordic aquatic fulvic acid (NAFA) were all standard humic materials obtained from the International Humic Substance Society (IHSS, St. Paul, MN) and used as received. Leonardite humic acid (LHA) was originally acquired as a crude blend from Horizon Ag Products (Kennewick, WA), under the trade name Agri-Plus. It was then subjected to the extraction procedure outlined by the IHSS [15]. Only the extracted form of LHA was used for this work. Aldrich humic acid (AHA), obtained from Aldrich Chemical Co. (Milwaukee, WI), was used as received. The following reagents were purchased from Fisher (Pittsburgh, PA) and used as received: KCl,  $\text{ZnCl}_2$ ,  $\text{NH}_4\text{OH}$ , and  $\text{PbCl}_2$ . Other analytical grade reagents used as received include,  $\text{CdCl}_2$  (EM Science, Cherry Hill, NJ), and  $\text{CuCl}_2$  (Mallinckrodt Chemical Works, St. Louis, MO).

Solutions (50 ppm) of the humic substances were prepared by placing the material in water, followed by the drop-wise addition of  $\text{NH}_4\text{OH}$  until dissolution could be seen to occur. The solutions were then shaken until material was completely dissolved, purged with  $\text{N}_2$  for 10 min, and brought to volume. They were stored at room temperature. Stock salt solutions were also prepared (0.05 M) and stored at room temperature. All aqueous solutions were prepared with dou-

bly deionized water, treated with a 0.22  $\mu\text{m}$  Millipore filter system to a resistivity of at least 16  $\text{M}\Omega\text{ cm}$ .

### 2.2. Instrumentation and procedures

Conductivity measurements were made with a model 3082-series Multi-Function Conductivity Meter (Amber Science Inc., Eugene, OR), equipped with a 4-wire Au dip cell with a cell constant of  $10.00\text{ cm}^{-1}$ . The instrument was operated in the Auto Range mode, in which a cell drive sine wave in the range 33–31,000 Hz was automatically selected. Since all conductance values encountered were in the 0–2  $\mu\text{S}$  range, the frequencies implemented were 33 or 130 Hz, with an amplitude of 1.6 V rms and a midrange current of either 0.264 or 2.64  $\mu\text{A}$ . Measurements were taken at two different temperatures, 20 and 60  $^\circ\text{C}$ , and two different volumes of added salt solution, 40 and 150  $\mu\text{l}$ . These aliquots were added by means of an automatic Rainin micropipette to 20.0 ml of HA/FA solution under constant stirring, and the conductivity readings were immediately captured with a data logger at 25 ms intervals for a period of 140 s. An identical procedure was used with  $2.97 \times 10^{-4}\text{ M}$  KCl reference solutions. All solutions were contained in water-jacketed cells attached to a thermocirculator.

Dynamic light scattering measurements were taken with a Coulter N4 Plus submicron particle analyzer, equipped with a 10 mW Helium-neon laser with  $\lambda = 632.8\text{ nm}$ . The concentration of aqueous humic materials was 50 ppm, and salt solutions were added as described above; ca. 24 h was allowed for equilibration before measurement. All measurements were taken at a 90 $^\circ$  detection angle, and reported as averages of 10 sequential runs of 300 s. Calibration of the instrument was performed with polystyrene beads in the 50–500 nm size range. The instrument software was used in the *Unimodal* analysis mode, which displayed results as a Gaussian distribution with a peak values representing the weighted averages of aggregate sizes [16].

## 3. Results and discussion

To allow for a meaningful assessment of the dynamic conductivity measurement carried out here, a quasi-blank was included for each metal ion considered. This reference solution contained an inert electrolyte (KCl), which was subjected to the same measurement regimen as the HA solution, i.e. an aliquot of salt (e.g.  $\text{CuCl}_2$ ) solution was added under constant stirring and the conductivity was followed until it reached a steady value. The conductivity–time curve of the blank was then subtracted point-by-point from the one obtained with the HA solution. This process was found to eliminate mechanical mixing effects from the resulting difference curve. It also allowed for comparison of measurements with different metal salts in the same HA solution as differences arising from different ionic conductivities of the cations themselves were canceled out by the procedure.

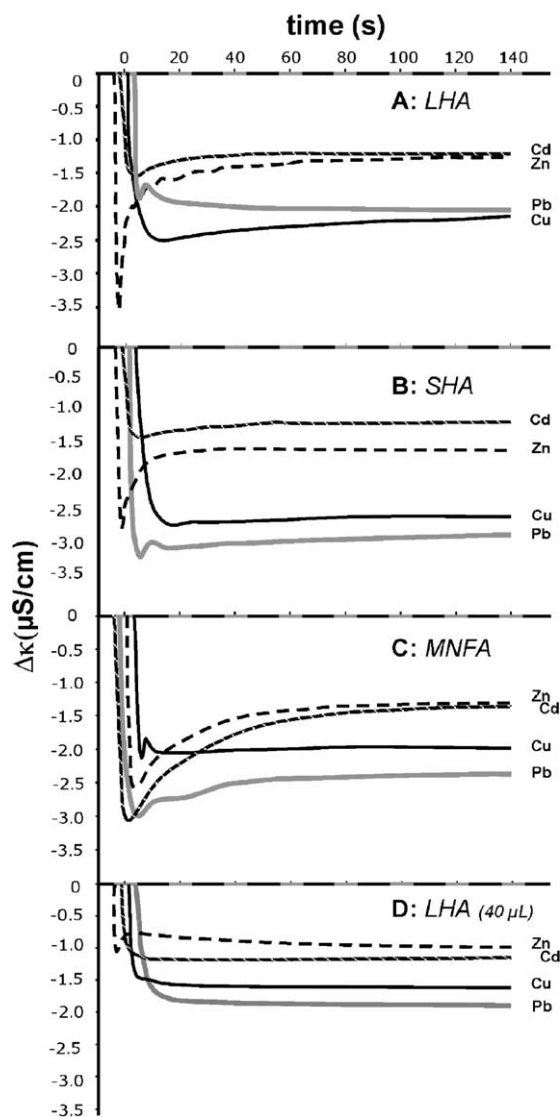


Fig. 1. Development of conductivity in humate and fulvate solutions upon addition of metals. (A–C) 150  $\mu$ l of 0.05 M metal chloride was added to 20 ml of 50 ppm HS solution; (D) 40  $\mu$ l of metal chloride was used. Curves are offset horizontally for clarity.

Typical results of the process described above are shown in Fig. 1. From the final solution conductivities (horizontal portions) in Fig. 1A, it is clear that dissolved LHA affected the relative mobility of each cation differently. The mobilities of all metals were reduced by the presence of the humate, but less so for Cd and Zn than for Pb and Cu. Fig. 1B and C show that this grouping was retained in the other humate solutions, albeit to somewhat different degrees. There can be two reasons for this: (i) the association of humate with Zn and Cd was weaker than its association with Pb and Cu, leaving relatively more free  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  in solution; (ii) the humate–metal complexes formed with Cd/Zn were smaller and hence more mobile.

All conductivity–time curves shown in Fig. 1 begin with a steep negative excursion, which in some cases became a peak

by a subsequent relaxation to higher solution conductivity. In the LHA and SHA solutions, this peak was especially pronounced with Zn, while Cd showed it to a lesser extent. In the MNPFA solutions, strong negative peaks appeared with all metals except Cu. When the relative amount of added metal salt solution was reduced from 150 to 40  $\mu$ l, only Zn showed evidence of a peak in the LHA solution (Fig. 1D).

The negative excursions of the  $\Delta\kappa$ – $t$  profiles in Fig. 1 are an indication of strong initial retardation of the metal ions in the humate solution relative to a KCl solution. The presence of a negative peak indicates that the metal–humate associations causing this (which are likely to be coulombic in nature) did not survive the dispersal of the added metal in the mixing process, and eventually yielded solutions with relatively high cation mobilities. This effect was found to be most pervasive with Zn and least so with Cu. This suggests that Zn–humate electrostatic interactions were important only at high local concentrations of the metal and did not produce complexes that were as strong and persistent as those formed with Cu. This is further borne out by the fact that a reduction of metal concentration relative to humate (Fig. 1D) produced a (relatively small) peak only with Zn. The prevalence of peaks obtained with fulvate solutions (MNFA, Fig. 1C) indicates that the initial metal associations of this material were generally less persistent than those formed in humate solutions. Cu was the exception.

The  $\Delta\kappa$ – $t$  curves obtained with Cu and Zn and a number of humic and fulvic acids are summarized in Fig. 2, which underscores the difference between the metals. Conductivity relaxation is shown to be strong with Zn and minimal with Cu. In accordance with this, the final relative solution conductivities with Cu were always lower than those with Zn, indicating stronger Cu associations with the organic polyanions. The average size of the humic aggregates brought about by the presence of Cu, as compared to Zn, may also play a role.

The influence of metal-induced aggregation on humic particle size has been reported [16,17]. Aqueous humates tend to aggregate even in the absence of metals, depending largely on the pH of the solution and hydrophobic interactions that exists between polymer chains. The presence of metal cations inevitably leads to further interactions that usually result in the formation of a visible colloid and eventual flocculation at sufficiently high ionic strengths. It has been suggested that the role of metal ions in humic interactions may be both intramolecular and intermolecular [18]. The former leads to contraction of the particle, while the latter has the opposite effect as it joins particles together.

In the work described here, the addition of metal ions to the humate/fulvate solutions undoubtedly led to changes in aggregation that influenced the final conductivities. Dynamic light scattering measurements of a 50 ppm LHA solution revealed an average humate particle diameter of ca. 250 nm. The addition of  $2.5 \times 10^{-4}$  M  $\text{Zn}^{2+}$  to the solution reduced this to about 130 nm. In contrast, the addition of a similar concentration of  $\text{Cu}^{2+}$  expanded the mean particle size to



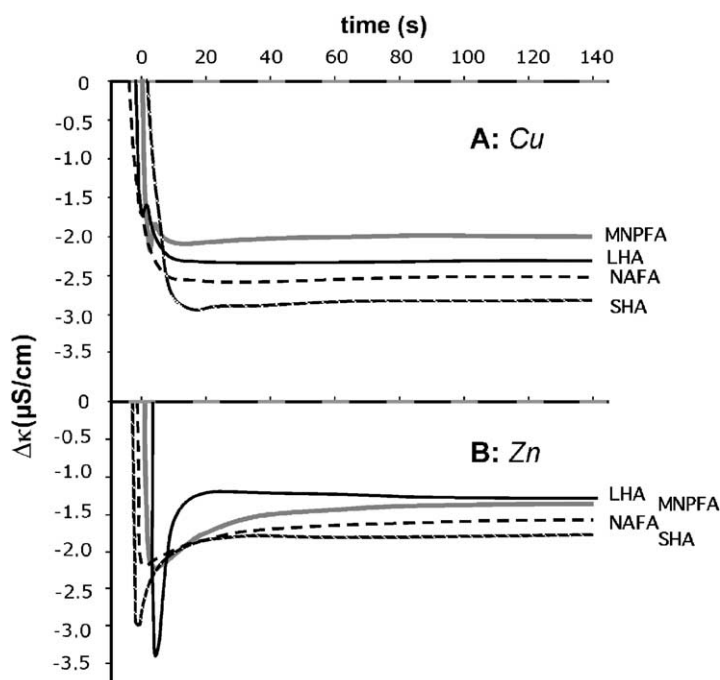


Fig. 2. Development of conductivity in humate and fulvate solutions upon addition of Cu and Zn. Conditions as described in Fig. 1.

590 nm. While this cannot be related to transitory interactions that produced the peaks in the  $\Delta\kappa$ - $t$  plots, it is relevant to the final solution conductivities shown in Fig. 1: the values for Zn were higher than those for Cu, which is consistent with the larger size of the Cu-induced humic aggregate. In addition to this, however, the stability of the metal-humate complex continued to play an important role, especially in regard to the peaks in the  $\Delta\kappa$ - $t$  curves. Stability constants reported for Cu complexes of humic substances are generally greater than those of the corresponding Zn complexes [19]; for instance, Nifant'eva et al. [20] reported a value of  $\log K = 5.4$  for the Cu complex of their humic isolate, while the corresponding value for the Zn complex was 4.7. This general observation is consistent with the concept that  $\text{Zn}^{2+}$  ions gain mobility upon dispersal through the humate solution, leading to the relaxation phenomenon described above.

#### 4. Temperature effects

As the conductivity behavior reported here is based on metal-humate associations, and the stability constants of the complexes formed tend to decrease with temperature, it should be expected that elevated temperature would lead to increased solution conductivities. The  $\Delta\kappa$ - $t$  curve for Cu with humates and fulvates at 60 °C (Fig. 3), however, showed surprisingly strong negative excursions having magnitudes that were more than three times as large as those shown in Figs. 1 and 2. Other metals gave similar curves, and peaks virtually disappeared. Higher temperatures, rather than producing solutions with greater ionic mobilities, appeared to give the opposite effect. The explanation for this observation may be found in the clouding effect that has been previously reported for HA solutions [21,22].

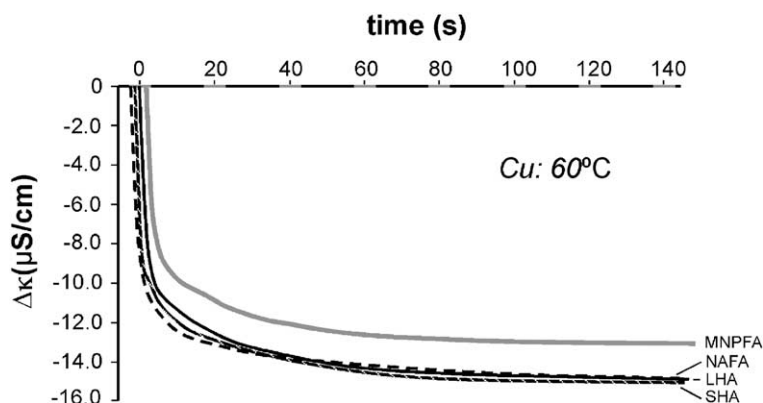


Fig. 3. Development of conductivity in humate and fulvate solutions upon addition of Cu at 60 °C. Other conditions as described in Fig. 1.

It was noted that HA solutions at slightly elevated ionic strengths, showed temperature induced clouding. This phenomenon, which is known from nonionic surfactant chemistry [23,24], manifests itself through phase separation (“clouding”) upon heating. It is generally ascribed to the reduction of dielectric constant of water with temperature, which leads to a decrease in hydration and the growth of micellar surfactant aggregates. These eventually become large enough to scatter visible light.

In the case of HA polyanions with added electrolyte, the effect involved a gradual growth of humic aggregates as the solution was heated. In some instances this produced a slight Tyndall effect, but always led to the formation of larger aggregates, even when the solution appeared homogeneous. The reduced mobility of these larger species (cf. the particle size effect expressed in Eq. (6)), as well as their enhanced ability to accommodate (condensed) counter ions, accounts for relatively low conductivity of the resulting solution.

The results described here indicate that metal solutions entering bodies of water that contain relatively low concentrations of humic materials interact with these substances to different extents. In the case of copper, associations with both humates and fulvates appeared to be strong and rapid and remained largely intact upon dispersal after initial contact. At the other extreme, zinc interacted strongly as long as its local concentration was high, but the associations declined upon dispersal. In all cases, metal ion mobility in the presence of fulvate was greater than with humates. Higher temperatures led to reduced ionic mobility. The measurements involved are simple, rapid, and potentially applicable to a large number of cationic species. They may be used to good effect in the assessment of initial impact of metal solutions entering natural waters containing small amounts of dissolved humic materials.

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